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Mechanisms of Comp-B Thermal Explosions

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Abstract. The LLNL-scaled thermal explosion experiment (STEX) was designed with numerous diagnostics in order to (1) capture the physics and chemistry of an explosive prior to thermal ignition and (2) quantitatively measure the violence post-ignition. With this abundance of diagnostics and supporting experiments, such as decomposition kinetics and deflagration rates, the mechanisms of thermal explosion can be better understood. Here we discuss recent experiments on Comp-B with an emphasis on the importance of vessel confinement strength and the inclusion of a vent hole in the vessel. Our discussion will highlight the pre-ignition mechanisms and provide insight into the mechanisms that dictate the violence of Comp-B and, possibly, other explosives.

Introduction

Understanding the chemical and physical mechanisms underlying a thermal explosion of an energetic material is important to safety assessment and accident prevention. These mechanisms are complex therefore experiments and modeling/simulations need to complement each other. At Lawrence Livermore National Lab (LLNL), our approach is to parameterize models with small experiments (e.g. <10g), validate these models with medium scale experiments (e.g. <1000g), and then predict thermal explosions using the model(s). To that end, the Scaled Thermal Explosion eXperiment (STEX) was developed as a high fidelity validation experiment for ALE3D thermal explosion models.

STEX is a medium scale experiment in which approximately 500-700 g of explosive is heated at a controlled rate (as slow as 1 °C/min) until explosion. The experiment is heavily diagnosed with embedded thermocouples, an embedded pressure sensor, external strain gauges, radar horns and photo-doppler velocimetry (PDV) for violence, and high speed video. The vessel is tightly sealed to prevent pre-ignition leaking (which can quench a thermal explosion in some cases) and provides an excellent study of thermal explosion pre-ignition phenomena and post-ignition violence. This experiment was described in detail previously,[1] however, as with any experiment, it has matured as diagnostics improve and scientific questions arise.

Comp-B is an important explosive because of its performance and the fact that it is melt-castable. The typical formulation consists of approximately 60% RDX and 40% TNT; sometimes wax is included in the formulation. Many have studied the thermal explosion of Comp-B, both because of its current use in various applications, and as a model system for other melt-castable explosives. To that end, LLNL performed a series of Comp-B thermal

explosion experiments and reported the results in 2002.[1] The previous STEX experiments on Comp-B used vessels able to confine the explosive up to 1 or 2 kbar (100 or 200 MPa), and heating rates of 1, 2, or 3 °C/min. The results of these experiments demonstrated that increasing confinement resulted in increased violence and increasing heating rate reduced the violence.

Because 1 or 2 kbar confinement pressure is much larger than what is typically found in real containers (e.g. storage containers), a study of Comp-B thermal explosions under lighter confinement was necessary. To that end, we performed two STEX experiments using a ½ kbar (50 MPa) confinement vessel; the first was hermetically sealed, and the second was allowed a small vent for pressure relief. Our results demonstrate that the vented experiment was significantly more violent than the hermetically sealed experiment, as will be discussed in detail.

Our experiments are not the first to investigate the influence of venting on the thermal explosion of Comp-B. Krawietz et al. at the Air Force Research Laboratory investigated the thermal explosion mechanism of Comp-B in a 1L round bottom flask (i.e. glass) with an open neck.[2] Their results provide insight into the pre-ignition mechanisms of various formulations (variable amounts of TNT and RDX). However, the open neck in the vessel could allow for significant evaporation (and evaporative cooling) of TNT, thus their results may not be applicable to sealed vessel conditions. In addition, their post-ignition violence assessment was qualitative as they were only able to look at the explosion debris size of their wood-paneled oven. Their results are difficult to model, especially for violence metrics. Madsen et al. at Picatinny Arsenal performed a series of STEX-like experiments in which the top end-cap was deliberately drilled out with one or many holes in order to allow for venting.[3] Their experiments used a minimum number of diagnostics (i.e. video at 30 fps, and post-explosion fragment assessment) and were not designed as a validation test for high fidelity modeling. In addition, their experiments utilized band heaters around the vessel wall that may change the wall strength in uncharacterized ways, making it difficult to model or understand the violence based on fragment distributions. Based on these previous experiments, it was clear that light confinement and vented experiments would be quite interesting. Because our experiment is heavily diagnosed, the results are extremely useful for model validation work. Finally, because we can directly compare our results to heavily confined STEX experiments, we can gain new insights into the role of confinement and hermaticity in a thermal explosion.

Experimental

The STEX design was detailed in previous publications;[1] however, because of maturing diagnostic capabilities, there have been some changes that will be discussed briefly here. The vessel is made of 4130 steel; the inner dimensions are 2 inches diameter x 8 inches tall. Diagnostics described previously include: a five-junction internal thermocouple probe, a pressure gauge, four strain gauges on the vessel exterior, numerous RTD temperature probes on the vessel exterior, and radar horns to measure fragment velocities after the explosion. New diagnostics include photo-doppler velocimetry (PDV) probes and high speed video (150000 fps or 6.67 μs/frame). The vessel is heated via three IR lamps around the cylinder walls and stove top heaters on the top and bottom flange to prevent heat loss at the ends of the charge. Figure F1 shows a photo of a fully assembled STEX experiment before explosion.

Two experiments were performed, labeled TE-66 and TE-67. TE-66 was hermetically sealed and includes all the diagnostics described above. TE-67 was identical to TE-66 except that the pressure sensor was removed and replaced with a vent-tube and overflow spill cup. In both experiments Comp-B (LLNL lot C-377, shipped from Dyno Inc. in 1999) was cast directly into the vessel (TE-66 used 640.0 g, TE-67 used 639.7g) leaving 39.8 cm^3 or 9.7% ullage at room temperature. This ullage was designed to allow for thermal expansion of the materials during heating. In both experiments, the vessel was heated rapidly to 130 °C then ramped at 1 °C/min until explosion. Differential scanning Calorimetry (DSC) experiments were performed on sub-milligram quantities at various heating rates using pin-hole pans using TA Instruments M2920. High pressure strand burner experiments are described

elsewhere[4] and the results for heated Comp-B are presented here. Strand burner towers were prepared by loading 8 pressed Comp-B pellets (1/4" diam. X 1/4" tall) into a Teflon cup. Burn wires were threaded through small holes in the walls of the cup. The cup was machined out to diameter that allowed for 10% expansion of the pellets as they melted. Samples were heated slowly to desired temperature (ca. 1.5 C/min), held for 2 hours and ignited while still hot.

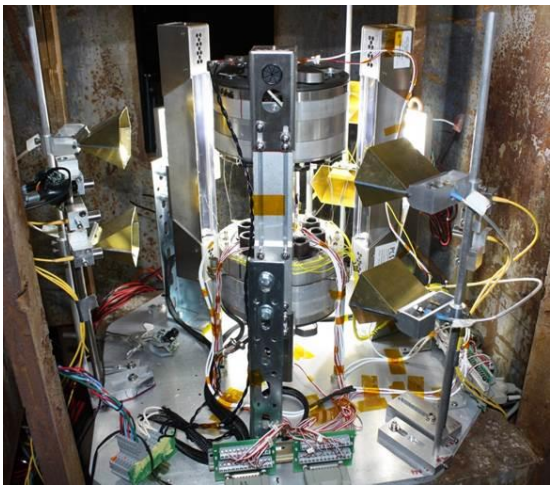

Fig. F1. Pre-explosion image of STEX experiment (TE-66 shown here, TE-67 looks very similar)

Results and Discussion

TE-66

Figure F2(a) shows the internal temperature during the final hours of the experiment. As expected, the material is hottest at the center. Upon closer inspection, one can see a slope change in the internal temperatures at 152 °C (for the middle TC), most likely due to self-heating (see also Figure F2(b)). At 162 °C the internal temperature surpasses the external wall temperature and the thermal runaway and explosion follows shortly afterwards. It is notable that in the final stages (i.e. $>165 \times 10^3$ sec), the thermocouple readings shift from smooth to jagged or bumpy. In solid explosives, these temperature readings remain relatively smooth all the way to thermal explosion, hence we hypothesize that the liquid inside the vessel may be bubbling or frothing in these last stages creating temperature spikes and or dips. Vessel strain and internal pressure were measured but results were unremarkable and are omitted here due to space constraints.

High speed video of the explosion is, perhaps, the most revealing. Figure F3 shows stills of the video. At about -826 µs a brown cloud of debris or explosive appears on the right side of the image (circled in red). The timing of the debris appearance is generally well correlated with the peak pressure at -875 µs (see Figure F4).

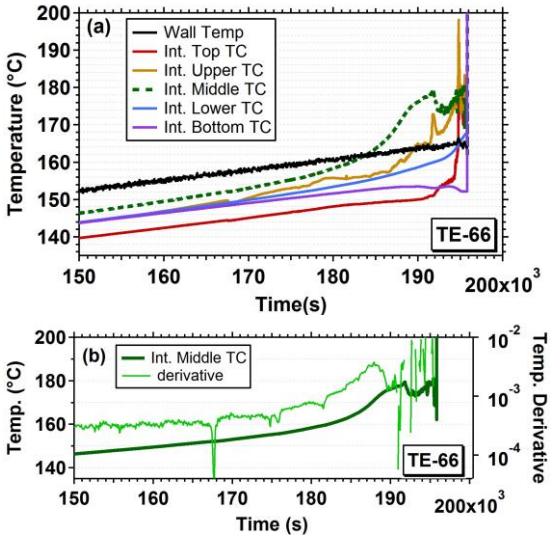

Fig. F2. (a) TE-66 internal temperature profile and (b) derivative of middle TC showing slope changes.

One would expect some lag between vessel rupture and debris appearance and since the first rupture occurs out of view from the camera, there will be extra transit time as the debris moves into the field of view. As time progresses, the debris cloud expands and the vessel wall begins to unwrap and fly to the left side of the image. Notably absent from all these images is any burning explosive, in fact, the high speed video images are somewhat dark because in set-up we were expecting light from the burning explosive. This video suggests that the material never reached full thermal explosion and burn. Based on the thermocouple data, it seems most likely that the material was just starting to thermally runaway

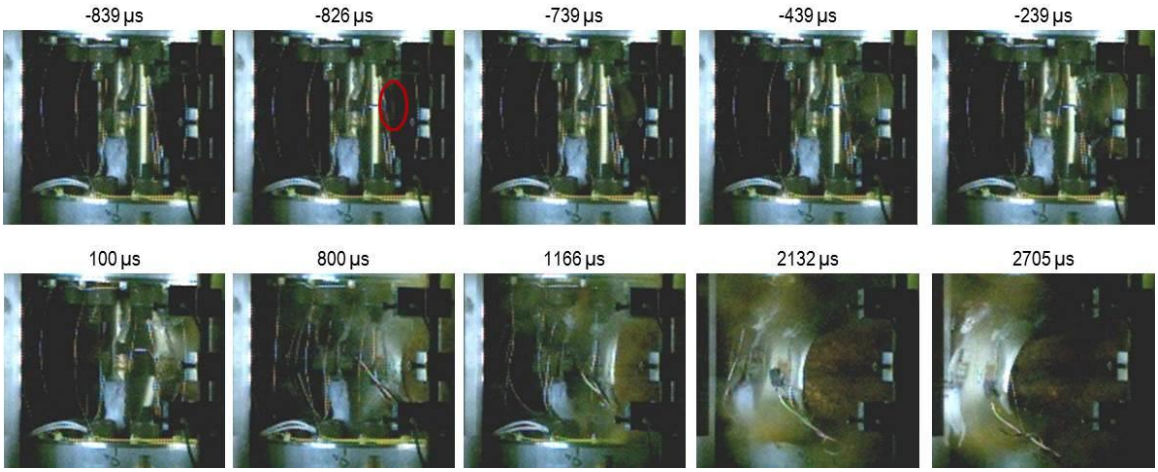

Figure F3. High speed video frames during thermal explosion of TE-66. Red circle designates debris.

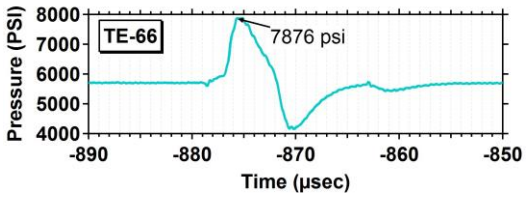

Fig. F4. Fast-scan pressure results for TE-66.

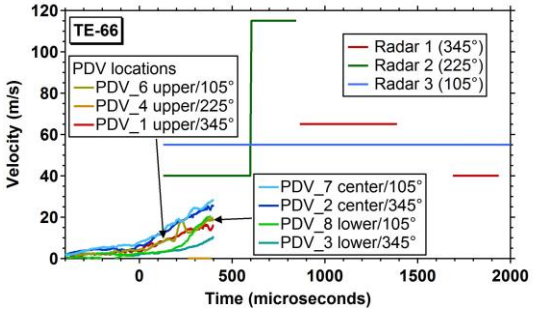

Fig. F5. PDV and radar results for TE-66.

and the pressure reached the confinement pressure of the vessel causing a burst.

The violence in this experiment was very low. PDV results consistently showed a maximum wall velocity of 30 m/s or less and Radar reported a maximum fragment velocity of 115 m/s (see Figure F5). Previous experiments with a 2 kbar vessel reported Radar measurements as high as 2800 m/s.[1] A post-experiment photo is shown in Figure F6; it reveals minimal damage. In

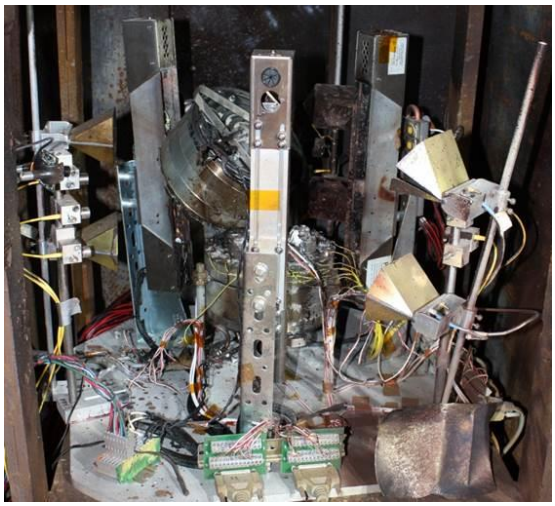

Fig. F6. TE-66 Post Expt. Note vessel wall was placed in the in the lower right hand corner of the photo.

comparison, a destructive explosion will reduce the whole assembly to a heap of small fragments and shattered endcaps and flanges (see Figure F9 for example).

TE-67

In TE-66, we observed the vessel rupture before it was able to reach full thermal explosion. The remaining question in this series of confinement experiments, which includes the 1

and 2 kbar experiments done previously, was how the material would behave when confined but not hermetically sealed. In order to address this question, we decided to set up TE-67 with a small vent.

The vent was introduced by replacing the pressure sensor with a "cup" mounted on a long tube. We had hoped that the tube would only vent gases; however, photos of the cup-reservoir during the experiment revealed significant liquid accumulation prior to thermal explosion. By our estimates, the cup contained about 80 mL of explosive in the final photo before explosion (not shown).

Figure F7 shows the internal and wall temperatures in the final stages of the experiment. Throughout the experiment, and in particular, at thermal runaway, the middle temperature remains the hottest. At T=198 × 10^3 sec, when the middle TC hit 154 °C, the interior temperature slope changed, most likely due to self-heating. At the same time/temperature, three of the five interior temperature profiles (upper, middle, and lower) transitioned from smooth to jumpy, eventually the top and bottom temperature profiles also became jumpy. As discussed in the TE-66 section, this jumpiness may be indicative of bubbling and frothing of the material. At 163 °C the interior temperature exceeds the exterior wall temperature, and about two hours later the vessel explodes.

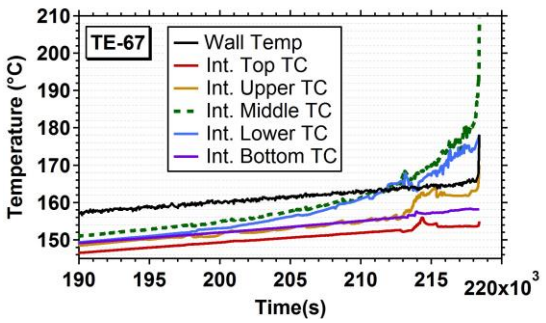

Fig. F7. TE-67 internal temperature profile.

High speed video shows two explosions; both are shown in Figure F8 in a series of frames. At -180 µs we can first see the first flames appear, indicating that the vessel has started to break open. The fireball grows and saturates the camera at about 58 µs and begins to recede at about 418 µs. At about 830 µs the flames appear to be dying down but there is a second fireball at ca. 1400 µs that ramps up until the camera cuts out at 1804 µs. This second explosion could be the bottom portion of the charge exploding, or may be due to hot projectiles (e.g. vessel fragments or unreacted explosive) hitting the heater lamps and exploding.

From the high speed video it is evident that the break-out began in the upper portion of the vessel. However, the thermocouple results clearly show the ignition at the center of the charge. It seems plausible that the burn propagated up from the center; especially since there may have been more partially decomposed/reactive gases in upper portion of the vessel allowing for more convective flame spread.

The PDV and radar results indicate that in general the explosion was not very violent (see Figure F9). PDV peak velocity was 417 m/s and radar peaked out at 900 m/s. In contrast, the post-experiment fragment analysis indicates that the reaction was extremely violent.

Figure F10 shows pre- and post-experiment photos, in the post-experiment the shot-stand was mostly empty and much of the vessel and diagnostics were reduced to small fragments. The vessel end-cap and flange assemblies are also shown in Figure F10 and the damage observed was on par with the more violent 2 kbar stex experiments.[1] The top end-cap and flange are still attached to each other and relatively unscathed. The bottom flange was detached from the endcap (which is only achievable by shearing off all the bolts) and broken into 6 pieces. The bottom endcap center portion (the portion that was in contact with the explosive) was partially punched out. Keeping in mind that the flange and endcap are both 1 inch thick steel (hardened 4130), one can surmise that the explosion of the bottom portion of the charge was very violent. PDV and radar are unable to quantify this violence because they are destroyed early in the explosion (ca. -80 µs). In fact, both PDV probes mounted on the lower portion (light green and dark green) indicate almost no wall velocity before they cut out. Based on the damage to the bottom endcap/flange, we know there must have been substantial wall velocities at some point in the explosion. Hence, we believe the secondary fireball observed in the high-speed video at ca. 1400 µs is most like the

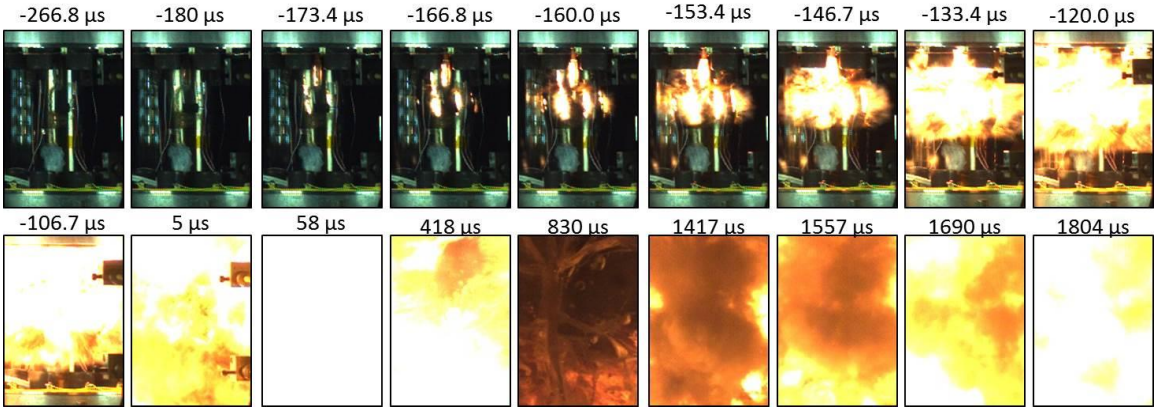

Fig. F8. High speed video frames for TE-67. Vessel can be seen to expand between -266.8 and -180 µs.

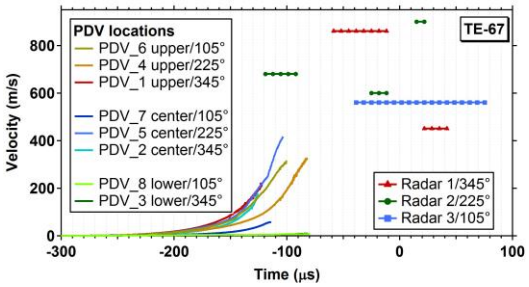

Fig. F9. PDV and Radar results for TE-67.

explosion of the bottom half of the charge.

The thermal explosion locations and violence could be explained by the distribution of material within the charge just prior to explosion. According to our records, this lot of Comp-B is a waxless formulation with 60% RDX and 40% TNT (analytical testing is underway to precisely characterize the percent of each constituent). At elevated temperatures, the TNT is liquid and some of the RDX has dissolved into the liquid TNT.[5] Asthe temperature continues to rise, one would expect some decomposition of TNT and RDX to begin producing reactive transient species. Because the transient species are fragments of RDX and TNT they should have lower density and, hence, migrate up. In addition, the undissolved RDX crystals may settle as the TNT melts. Therefore, we hypothesize that in the final minutes or seconds before thermal explosion, the explosive is very heterogeneous from top to bottom. The bottom is likely to be RDX rich and rather dense; as we move up the charge, the TNT concentration will likely rise and near the top the explosive is TNT rich and may be frothy or bubbly. Because we displaced nearly 80 mL of explosive from the vessel into the cup, there must be space in the vessel top that is occupied by gases. In addition, the displaced explosive is

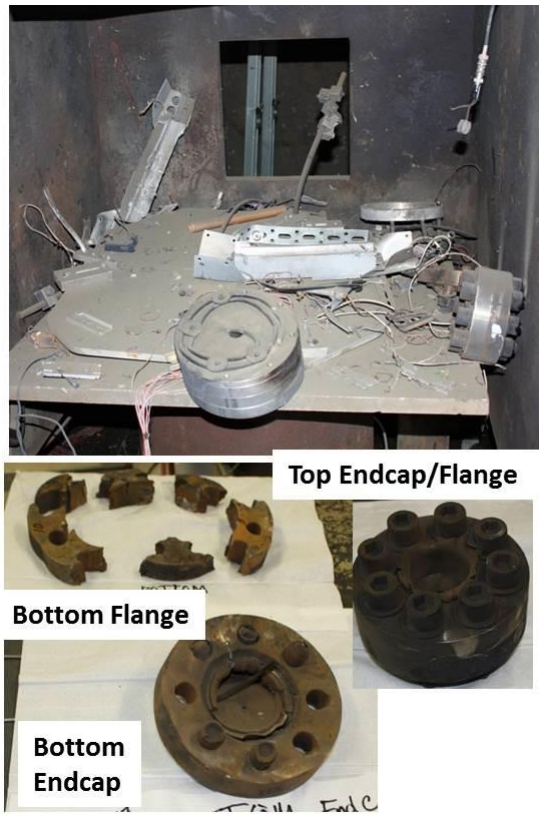

Fig. F10. Post-experiment photos reveal extensive damage of TE-67 experiment.

mostly TNT so the material in the vessel is RDX-rich.

If this picture of the explosive prior to ignition is correct, one can hypothesize that the flame spreads up from the center ignition point quickly via convective heat-transfer mechanisms. Hence the vessel appears to rupture in the upper portion, but the internal thermocouples indicate that the ignition zone (i.e. the hottest zone) was in the center of the charge. Once the vessel ruptures, the only material left to consume is in the bottom half of the vessel. The pressure and temperature rise from the initial burn and explosion may help drive the burn down into the bottom. Because RDX is a more violent and reactive material compared to TNT, and because the bottom is likely to be RDX rich, it is logical that the bottom of the vessel experienced so much more damage than the top. This mechanism is hypothesized, but further characterization of the nature of the material prior to ignition is necessary to fully understand the mechanisms underlying this STEX experiment.

Complimentary DSC and Strand Burner Results

It is notable that in both TE-66 and TE-67 the middle internal thermocouple begins to ramp up in temperature at just above 150 °C. DSC results shown in Figure F11 reveal the onset of an endothermic process at ca. 145 °C. By 150 °C this endothermic process is well underway. This endotherm could be the melt of RDX or, more likely, the dissolution of RDX into molten TNT. DSC of neat-RDX reveals an RDX melt of ca. 200 °C (not shown). Preliminary strand burner experiments at 100 °C, 125 °C and 150 °C show an interesting change in burn behavior at the highest temperature. Further work is necessary to validate the 150 °C strand burner results, however, it is likely that the change in burn behavior is correlated to the STEX observations at ~150 °C and the DSC results.

Summary and Conclusion

In summary, two different STEX experiments were performed in order to understand the role of confinement pressure and hermeticity on the mechanisms and violence of Comp-B thermal

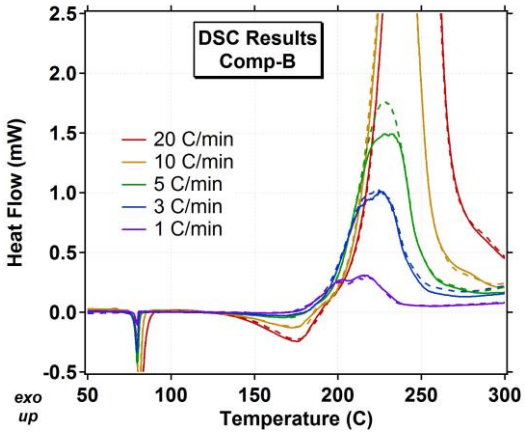

Fig. F11. DSC results on Comp-B at various heating rates.

explosions. These experiments were designed to complement previous STEX experiments that were performed at 1 and 2 kbar. In addition, it was our goal to quantify violence of these lightly confined or unsealed experiments and supply experimental data for validation of our ALE3D thermal explosion modeling.

The sealed ½ kbar experiment was interesting because it demonstrated how weakening the vessel strength can help to mitigate violence. When the interior pressure exceeded the vessel confinement, the whole vessel failed and the vent was very rapid. Because the material had not quite reached the burn stage, the damage was minimal. In designing safer casing materials, a vessel that can fail or release uniformly and quickly may be the best option for minimal damage.

The vented ½ kbar experiment was surprisingly violent. Our vent was designed to allow pressure equilibration during the heating stages but too restrictive during thermal explosion to allow for much mitigation of the violence. The vent worked as designed and the result was a violent explosion. Our hypothesis is that the material was allowed to fully ignite in the vented experiment and once ignited, produced a violent explosion.

One general question that remains is whether venting other explosives will enhance or mitigate violence. Our previous STEX experiments on HMX-based formulations indicate that a vent or leak does little to change the violence of the

explosive.[1] We hypothesize that in a solid explosive, if the ignition point is at the center of a charge, inertial confinement helps to contain the reactive gases and thermally insulate the ignition point. As such, a leak or vent on the vessel wall/seals will do little to change the explosion. In particular, as the pressure rises at the ignition point, inertial confinement prevents the pressure from pushing on the vessel walls or releasing via the vent. In contrast, if pressure rises at the center of a liquid charge, it is quickly transferred to the walls of the vessel. The pressure rise at the ignition point is either relieved via the vent or by pushing against the vessel walls. Based on this logic, one would surmise that many liquid explosives might be more violent if allowed a small vent, and may be mitigated via a substantial vent or an easily destroyed vessel wall. Further work on other liquid explosives would provide interesting insight into this hypothesis.

Acknowledgements

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Question, Laura Smilowitz, LANL: To what do you attribute the slope change observed at 150^{o}C?

Reply by: E.A. Glascoe: DSC results (Figure F11) and a discussion were included to answer this question. Most likely melting and dissolution of the RDX lowers the viscosity of the fluid and allows for more convective flow and accelerated decomposition of the RDX.

Question, Andrew Laing, QinetiQ: Please can you comment on the different event violence levels for identical shots #12 and #13?

Reply by E.A. Glascoe: These experiments are reported and discussed in Reference 1.

Question, Michael L. Hobbs, SNL: Do you see differences in flow behavior between confined and unconfined experiments? Could you put a camera in your experiment to better see the flow behavior?

Reply by E.A. Glascoe: The only indicators we have of fluid flow are the jumpy thermocouple results. While there are many differences between the particular responses of each thermocouple in TE-66 versus TE-67, there is no way to know whether these differences are due to the confinement of the vessel or just shot-to-shot variability. In general, a comparison of TE-66 and TE-67 suggest that the flow is similar in both experiments but diagnostics that are designed to measure flow might be able to resolve differences between confined and unconfined. A camera is possible and may be considered in future experiments.